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(54) **A aqueous suspension of a particulate calcium carbonate pigment**

Eine wässrige Suspension eines festen Kalziumkarbonatpigments

Une suspension aqueuse d'un pigment solide de carbonate de calcium

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FR-A- 2 468 688 **GB-A- 2 139 606**
GB-A- 2 200 104

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Description

This invention relates to suspensions of calcium carbonate pigments, to paper coating compositions formed from such suspensions and to coated paper made using said coating compositions, and to a paper-making process which includes the recycling of coated paper.

It is well known to use calcium carbonate both as a filler in the manufacture of paper, and as a pigment in the coating of paper.

It is known that calcium carbonate fillers can be cationically dispersed in water so that the particles have an overall positive charge (EP-A-0278602A), and that such cationically dispersed suspensions are useful in paper making because the need to use a cationic retention aid can be reduced or even eliminated.

It is further known that calcium carbonate pigments which have been treated to have specified particle size and surface area characteristics, can be anionically dispersed in water to form high solids paper coating compositions for gravure printing papers (GB-A-2139606A).

It is common practice for large quantities of paper to be recycled at the point of manufacture for one reason or another, the recycled paper being reduced into a fibrous state and then incorporated in a paper-making composition.

According to one aspect of the present invention there is provided a high solids, aqueous suspension of a particulate calcium carbonate pigment, characterised in that the particulate calcium carbonate pigment has a specific surface area, as measured by the BET N_2 method, of less than $7.5\text{m}^2\text{g}^{-1}$, and a particle size distribution such that not more than 1% by weight of the particles have an equivalent spherical diameter (esd) larger than 10 microns, at least 65% by weight of the particles have an equivalent spherical diameter smaller than 2 microns and not more than 10% by weight of the particles have an equivalent spherical diameter smaller than 0.25 microns; and in that the particulate calcium carbonate pigment is cationically dispersed with a dispersing agent which is a combination of a cationic polyelectrolyte and an anionic polyelectrolyte, with the cationic electrolyte being used in an amount sufficient to render the pigment particles cationic.

According to a second aspect of the present invention there is provided a paper coating composition which has a solids content of at least 45% by weight, characterised in that it comprises a high solids, aqueous suspension according to the present invention, and a non-ionic or cationic adhesive.

According to a third aspect of the invention there is provided a process for making paper which includes the step of recycling coated paper that has been reduced to a fibrous, recyclable state and then incorporated into a paper-making composition, characterised in that the coated paper is a paper which has been coated with a coating composition according to the invention.

A cationically dispersed, high solids, aqueous suspension of a calcium carbonate pigment in accordance with the present invention has very good rheological properties. In particular, it has been found that a cationic aqueous suspension, or slurry, having a given viscosity and prepared in accordance with the present invention can have a higher solids content than a slurry in which the calcium carbonate pigment has a broader particle size distribution.

A high solids, aqueous suspension according to the present invention should preferably have a solids content of at least 60% by weight solids.

The calcium carbonate pigment, when ground to a particulate mass, exists in the form of regular, approximately spherical particles having a low mean particle aspect ratio. The calcium carbonate may be in any form, natural or synthetic. Particularly preferred is ground marble, although precipitated calcium carbonate (PCC) and chalk are operable.

Preferably, the calcium carbonate pigment employed in the present invention should have a specific surface area, as measured by the BET N_2 method, which is less than about $6.5\text{m}^2\text{g}^{-1}$, but preferably is at least $2\text{m}^2\text{g}^{-1}$.

A calcium carbonate material is ground, before dispersion, to the desired particle size distribution. The grinding conditions can be adjusted in a manner known per se to produce pigments having varying particle size distributions. Ground marble for use in the present invention is preferably formed by first crushing batches of marble in aqueous suspension in the absence of a chemical dispersing agent using a particulate grinding medium. Further size reduction can be achieved by dewatering the suspension of ground marble, for example by filtration in the absence of a flocculating agent, and then drying the pigment, and pulverising the dried product in a conventional mill.

Where the calcium carbonate material carries a neutral or positive charge, such as marble, the particles of the pigment may be readily dispersed using a dispersing agent, in accordance with the invention, comprising a combination of an anionic polyelectrolyte and a cationic polyelectrolyte, the cationic polyelectrolyte being used in an amount sufficient to render the particles cationic. However, chalk particles, when in a raw state, do not carry a positive charge, because of natural anionic species absorbed to the particle surface, and the chalk particles should be subjected to vigorous agitation in order to strip off such anionic species and render the particles capable of being effectively dispersed at high solids using the combination of an anionic polyelectrolyte and cationic polyelectrolyte.

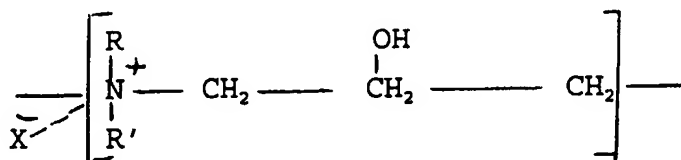
In the method of making the aqueous suspension, or slurry, of the invention, it is normally the case that the raw pigment is received as a filter cake having a relatively high solids content. To this is added the dispersing agent in order

to provide a dispersed high solids slurry (45-80% by weight solids) which may then be subjected to vigorous mixing.

The particulate calcium carbonate pigment is dispersed with a combination of an anionic polyelectrolyte and a cationic polyelectrolyte, with the cationic electrolyte being used in an amount sufficient to render the pigment particles cationic. Generally, the amount of cationic polyelectrolyte used is in the range of from about 0.01% to about 1.5% by weight, based on the dry weight of calcium carbonate, and the amount of anionic polyelectrolyte used is such that the weight ratio of the cationic polyelectrolyte to anionic polyelectrolyte is in the range of from about 2:1 to about 20:1.

Preferably, the anionic polyelectrolyte is a water-soluble vinyl polymer, an alkali metal or ammonium salt thereof or an alkali metal or ammonium salt of polysilicic acid. Most preferably, the anionic polyelectrolyte is a poly(acrylic acid), a poly(methacrylic acid), a substituted poly(acrylic acid) or a substituted poly(methacrylic acid), or an alkali metal or ammonium salt of any of these acids. The substituted poly(acrylic acid) may be a partially sulphonated polymer. An especially effective anionic polyelectrolyte is an alkali metal or ammonium salt of a copolymer of acrylic acid and a sulphonic acid derivative of acrylic acid, in which the proportion of the sulphonic acid derivative monomer is preferably from 5% to 20% of the total number of monomer units. The number average molecular weight of the anionic polyelectrolyte is preferably at least 500, but preferably no greater than 100,000. The amount used is generally in the range of from about 0.01% to about 0.5% by weight based on the weight of dry pigment, and preferably is in the range of from about 0.1 to 0.2% by weight.

The cationic polyelectrolyte may be a water-soluble substituted polyolefin containing quaternary ammonium groups. The quaternary ammonium groups may be in the linear polymer chain or may be in branches of the polymer chain. The number average molecular weight of the substituted polyolefin is preferably at least 1500 but preferably no greater than 1,000,000, and is more preferably in the range of from 50,000 to 500,000. The quantity required is generally in the range of from about 0.01% to about 1.5% by weight based on the weight of dry pigment. Advantageous results have been obtained when the substituted polyolefin is a poly(diallyl di(hydrogen or lower alkyl)ammonium salt). The lower alkyl groups, which may be the same or different, may have, for example, up to four carbon atoms and each is preferably methyl. The ammonium salt may be, for example, a chloride, a bromide, an iodide, HSO_4^- , CH_3SO_4^- or nitrite. Preferably, the salt is a chloride. Most preferably, the cationic polyelectrolyte is poly(diallyl dimethyl ammonium chloride). Alternatively, the water-soluble substituted polyolefin may be the product of copolymerising epichlorohydrin and an aliphatic secondary amine, said product having the formula



in which R and R', which may be the same or different, are each hydrogen or a lower alkyl group having from one to four carbon atoms, preferably methyl or ethyl and X is Cl^- , Br^- , I^- , HSO_4^- , CH_3SO_4^- or nitrite. The preferred number average molecular weight of this epichlorohydrin product is in the range of from 50,000 to 300,000.

Alternatively, the cationic polyelectrolyte may be a water-soluble organic compound having a plurality of basic groups and preferably having a number average molecular weight of at least 10,000 but preferably no greater than 1,000,000. Most preferably, the number average molecular weight is at least 50,000. These water-soluble organic compounds may be described as polyacidic organic bases, and are preferably compounds of carbon, hydrogen and nitrogen only and are free of other functional groups, such as hydroxy or carboxylic acid groups, which would increase their solubility in water and thus increase the likelihood of their being desorbed from the mineral in an aqueous suspension. Preferably, the organic compound is polyethyleneimine (PEI) having a number average molecular weight in the range 50,000 to 1,000,000. A further example of a water-soluble organic compound which may be employed is a polyethylene diamine which may be a copolymer of ethylene diamine with an ethylene dihalide or with formaldehyde.

The cationic polyelectrolyte is employed in an amount sufficient to render the mineral particles cationic. Experiments have shown that the zeta potential of the particles will normally be at least +20mV after treatment, typically in the range of from +30 to +40 mV and usually no greater than +50 to +60mV. These potentials have been measured using a dilute (0.02 weight %) solids suspension using a supporting electrolyte of potassium chloride (10^{-4}M) with a "Pen Kern Laser Z" meter.

The ratio, by weight, of cationic polyelectrolyte to anionic polyelectrolyte used is generally in the range of from about 2:1 to about 20:1, and preferably is in the range of from 2:1 to 10:1.

The calcium carbonate pigment is preferably mixed with the anionic polyelectrolyte before mixing with the cationic polyelectrolyte. This appears to enable a more fluid suspension to be obtained at a higher solids concentration.

Aqueous suspensions of the present invention should preferably be subjected to vigorous mixing before or after

dispersion of the pigment. Typically, the vigorous mixing should be sufficient to impart at least 10kJ energy per kg of the inorganic material, but preferably no more than about 50kJ per kg. Normally, the amount of energy input will be in the range of from 18-36kJ per kg of the inorganic material.

The high solids aqueous suspension of the present invention can be "made down" into a paper coating composition by dilution (if necessary) to a solids concentration of at least 45% by weight and by addition of an adhesive, which should be non-ionic or cationic in nature. Such adhesives contrast with the anionic adhesives which are normally used in paper coating compositions in which the pigment is anionic. Thus, cationic casein and cationic starch adhesives can be used as well as cationic or non-ionic latices. Such cationic and non-ionic adhesives are readily commercially available. The particular cationic or non-ionic adhesive used will depend, for example, on the printing process to be used, e.g. offset lithography requires the adhesive to be water-insoluble. For paper to be used in an offset printing technique, the amount of adhesive should preferably be of the order of from 7 to 25% by weight, based on the weight of pigment whilst, for gravure printing paper, the adhesive should be used in an amount of 4-15% by weight, based on the weight of pigment. The precise quantity of adhesive required will depend upon the nature of the adhesive and the material being coated, but this can readily be determined by the person skilled in the art.

The paper coating composition may also include other conventional paper coating composition adjuvants such as an insolubilising agent (e.g. a melamine formaldehyde resin), a lubricant such as calcium stearate and a catalyst to catalyze cross-linking of the cationic latex if present: a suitable such catalyst is sodium bicarbonate. The quantities of these adjuvants required are known to those skilled in the art. A full discussion of the constituents of paper coating compositions and of the methods of applying such compositions to paper is given in Chapter XIX, Volume III of the second edition of the book by James P. Casey entitled "Pulp and Paper: Chemistry and Technology". A further discussion is given in "An Operator's Guide to Aqueous Coating for Paper and Board", edited by T.W.R. Dean, The British Paper and Board Industry Federation, London, 1979.

The paper coating compositions of the invention can be used in a method of coating a sheet member using normal paper coating machinery and under normal paper coating conditions.

It has been found that the paper coated with a cationic paper coating composition in accordance with the present invention provides broadly similar results to that obtained with a conventional anionic system.

The coated paper which is obtained using coating compositions of the present invention is particularly suitable for use in a recycling process which includes the step of reducing the paper into a fibrous recyclable state and incorporating said fibre in a paper-making composition. Thus, a coated paper which is made using a coating composition of the present invention is of advantage when it is employed as "broke", or recycled paper, as part of a paper-making composition. Such a paper-making composition may include conventional paper-making pulp, such as a bleached sulphite pulp. Typically, the broke fibre and the conventional pulp will be employed in a ratio of from 10:90 to 60:40. Also included in the paper making composition will be a filler, for instance a calcium carbonate filler and also a retention aid. Since the broke fibre will include a proportion of calcium carbonate pigment from the coating, it is possible to reduce the amount of calcium carbonate filler employed to give a total quantity of filler in the range of from 5 to 20 percent by weight of the total paper-making composition. The weight of dried broke added (fibre and filler) should preferably be in the range of from about 5 to 30 percent by weight of fibre.

When the broke fibre employed is derived from a coated paper in accordance with the present invention, the amount of retention aid employed in the paper making composition can be reduced.

The advantages of using a paper, coated with a paper coating compositions of the present invention, in recycling are most important to the paper manufacturer.

The present invention will now be illustrated by the following Example:

EXAMPLE

Two calcium carbonate pigments were prepared by low solids sand grinding of marble flour. Adjustment of grinding conditions allowed products of varying widths of particle size distribution to be compared. Sedigraph data was obtained as shown in Table 1 below (percentages given are weight %):

Table 1

SAMPLE A		SAMPLE B	
0.3%	>10 μ m	0.8%	>10 μ m
75.5%	<2 μ m	70.2	<2 μ m
44.5%	<1 μ m	48.0	<1 μ m
20.0%	<0.5 μ m	28.5	<0.5 μ m
6.7%	<0.25 μ m	14.3	<0.25 μ m

Table 1 (continued)

SAMPLE A	SAMPLE B
Surface Area (BET N ₂)	
5.0m ² g ⁻¹	8. 6m ² g ⁻¹

Both samples were filtered to give a filter cake of between 70 - 75 % solids. This cake was then cationically dispersed using a pretreatment of sodium polyacrylate (Molecular weight 4000) followed by addition of a larger dose of polydadmac (i.e. a poly[diallyl dimethyl ammonium chloride]) of molecular weight - 500,000. The ratio of cationic to anionic polymer was maintained at between 3.2 and 3.5:1 by weight. Each suspension was diluted with water until a viscosity, measured at 100 rpm using a Brookfield Viscometer, of approximately 600 mPa.s was reached and the solids contents of the suspensions determined.

Table II

SAMPLE A - dispersion on high speed mixer			
Dose of anionic polyacrylate wt%	Dose of polydadmac wt%	Solids wt%	Brookfield viscosity mPa.s
0.11	0.36	70.3	600

Table III

SAMPLE B - Dispersion			
Polyacrylate dose wt%	Polydadmac dose wt%	Solids wt%	Viscosity Brookfield mPa.s
0.11	0.34	65.0	600
0.125	0.44	66.6	660
0.135	0.47	66.3	635

Hence in this example, a ground marble having a broad particle size distribution gives approximately 4 units lower solids for a given rheology when cationically dispersed.

Claims

1. A high solids, aqueous suspension of a particulate calcium carbonate pigment for paper coating compositions, wherein the particulate calcium carbonate pigment has a specific surface area, as measured by the BET N₂ method, of less than 7.5m²g⁻¹, and a particle size distribution such that not more than 1% by weight of the particles have an equivalent spherical diameter (esd) larger than 10 microns, at least 65% by weight of the particles have an equivalent spherical diameter smaller than 2 microns and not more than 10% by weight of the particles have an equivalent spherical diameter smaller than 0.25 microns; and in that the particulate calcium carbonate pigment is cationically dispersed with a dispersing agent which is a combination of a cationic polyelectrolyte and an anionic polyelectrolyte, with the cationic electrolyte being used in an amount sufficient to render the pigment particles cationic.
2. A high solids, aqueous suspension as claimed in claim 1, characterised in that the calcium carbonate pigment has a specific surface area, as measured by the BET N₂ method, in the range of from 2.0 to 6.5m²g⁻¹.
3. A high solids, aqueous suspension as claimed in claim 1, characterised in that the amount of cationic electrolyte used is in the range of from about 0.01% to about 1.5% by weight, based on the dry weight of calcium carbonate, and the amount of anionic polyelectrolyte used is such that the weight ratio of the cationic polyelectrolyte to anionic polyelectrolyte is in the range of from about 2:1 to about 20:1.
4. A high solids, aqueous suspension as claimed in claim 1, 2 or 3, characterised in that the aqueous suspension has been subjected to vigorous mixing, before or after dispersion of the calcium carbonate pigment, such that there is imparted to the suspension from 10 to 50 kJ of energy per kg of calcium carbonate.

5. A paper coating composition having a solids content of at least 45% by weight, characterised in that it comprises a high solids, aqueous suspension as claimed in claim 1, 2, 3 or 4, and a non-ionic or cationic adhesive.
6. A coated paper which includes a coating formed from a paper coating composition as claimed in claim 5.
7. A process for making paper which includes the step of recycling coated paper that has been reduced to a fibrous, recyclable state and then incorporated into a paper-making composition, characterised in that the coated paper is a paper as claimed in claim 6.

Patentansprüche

1. Wässrige hoch-feststoffhaltige Suspension eines teilchenförmigen Calciumcarbonatpigments für Papierbeschichtungszusammensetzungen, wobei das teilchenförmige Calciumcarbonatpigment eine spezifische Oberfläche hat, gemessen mit dem BET-N₂-Verfahren, von weniger als 7,5 m²g⁻¹ und eine Teilchengrößenverteilung, dass nicht mehr als 1 Gew.% der Teilchen einen Kugeläquivalenzdurchmesser (esd) größer als 10 µm haben, mindestens 65 Gew.% der Teilchen einen Kugeläquivalenzdurchmesser kleiner als 2 µm haben und nicht mehr als 10 Gew.% der Teilchen einen Kugeläquivalenzdurchmesser kleiner als 0,25 µm haben; und wobei das teilchenförmige Calciumcarbonatpigment kationisch dispergiert ist mit einem Dispersionsmittel, das eine Zusammensetzung aus einem kationischen Polyelektrolyten und einem anionischen Polyelektrolyten ist, wobei der kationische Polyelektrolyt in einer Menge verwendet wird, die ausreicht, die Pigmentteilchen kationisch zu machen.
2. Wässrige hoch-feststoffhaltige Suspension nach Anspruch 1, dadurch gekennzeichnet, dass das Calciumcarbonatpigment eine spezifische Oberfläche im Bereich von 2,0 bis 6,5 m²g⁻¹ hat, gemessen mit dem BET-N₂-Verfahren.
3. Wässrige hoch-feststoffhaltige Suspension nach Anspruch 1, dadurch gekennzeichnet, dass der kationische Elektrolyt in einer Menge verwendet wird im Bereich von etwa 0,01 bis 1,5 Gew.%, bezogen auf das Trockengewicht von Calciumcarbonat, und der anionische Polyelektrolyt in einer Menge verwendet wird, dass das Gewichtsverhältnis von kationischem Polyelektrolyt zu anionischem Polyelektrolyt im Bereich von etwa 2:1 bis etwa 20:1 ist.
4. Wässrige hoch-feststoffhaltige Suspension nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass die wässrige Suspension vor oder nach der Dispersion des Calciumcarbonatpigments stark gemischt wird, damit der Suspension Energie zugeführt wird zwischen 10 und 50 kJ/kg Calciumcarbonat.
5. Papierbeschichtungszusammensetzung mit einem Feststoffgehalt von mindestens 45 Gew.%, dadurch gekennzeichnet, dass sie eine hoch-feststoffhaltige wässrige Suspension nach Anspruch 1, 2, 3 oder 4 enthält und einen nicht-ionischen oder kationischen Klebstoff.
6. Beschichtetes Papier, das eine Beschichtung einer Papierbeschichtungszusammensetzung nach Anspruch 5 enthält.
7. Verfahren zur Papierherstellung, umfassend den Schritt des Wiederverwertens von beschichtetem Papier, das in eine faserförmige wiederverwertbare Form gebracht und dann in eine Papierherstellungszusammensetzung eingemischt wurde, dadurch gekennzeichnet, dass das beschichtete Papier ein Papier nach Anspruch 6 ist.

Revendications

1. Une suspension aqueuse à haute teneur en matières solides, d'un pigment particulaire de carbonate de calcium, pour des compositions de revêtement pour papier, dans laquelle le pigment particulaire de carbonate de calcium possède une surface spécifique, telle que mesurée par la méthode BET avec N₂, de moins de 7,5 m²g⁻¹, et une distribution de la taille particulaire telle que pas plus de 1% en poids des particules ont un diamètre sphérique équivalent (d.s.e.) supérieur à 10 microns, au moins 65% en poids des particules ont un diamètre sphérique équivalent inférieur à 2 microns, et pas plus de 10% en poids des particules ont un diamètre sphérique équivalent inférieur à 0,25 microns; dans laquelle le pigment particulaire de carbonate de calcium est cationiquement dispersé avec un agent dispersant qui est la combinaison d'un polyélectrolyte cationique et d'un polyélectrolyte anionique, l'électrolyte cationique étant utilisé dans une quantité suffisante pour rendre les particules de pigment cationiques.

2. Une suspension aqueuse, à haute teneur en matières solides, telle que revendiquée dans la revendication 1, caractérisée en ce que le pigment de carbonate de calcium possède une surface spécifique, telle que mesurée par la méthode BET avec N_2 , dans le domaine allant de 2,0 à 6,5 m^2g^{-1} .

3. Une suspension aqueuse, à haute teneur en matières solides, telle que revendiquée dans la revendication 1, caractérisée en ce que la quantité d'électrolyte cationique utilisée est dans le domaine allant d'environ 0,01% à environ 1,5% en poids, par rapport au poids sec du carbonate de calcium, et la quantité de polyélectrolyte anionique utilisée est telle que le rapport massique du polyélectrolyte cationique sur le polyélectrolyte anionique est comprise dans le domaine allant d'environ 2:1 à environ 20:1.

4. Une suspension aqueuse à haute teneur en matières solides, telle que revendiquée dans la revendication 1, 2 ou 3, caractérisée en ce que la suspension aqueuse a été mélangée vigoureusement, avant et après dispersion du pigment de carbonate de calcium, de sorte qu'on a conféré à la suspension 10 à 50 kJ d'énergie par kg de carbonate de calcium.

5. Une composition de revêtement pour papier ayant une teneur en matières solides d'au moins 45% en poids, caractérisée en ce qu'elle comprend une suspension aqueuse à haute teneur en matières solides, telle que revendiquée dans la revendication 1, 2, 3, ou 4, et un adhésif non ionique ou cationique.

6. Un papier revêtu qui comprend un revêtement formé à partir d'une composition de revêtement pour papier telle que revendiquée dans la revendication 5.

7. Un procédé pour fabriquer du papier, qui comprend l'étape consistant à recycler du papier revêtu qui a été réduit sous une forme fibreuse, recyclable, et qui a ensuite été incorporé à une composition de fabrication de papier, caractérisé en ce que le papier enduit est un papier tel que revendiqué dans la revendication 6.